



Review of Literature



Assam occupies 2.4% of India's land area and is known as a centre for biodiversity in Northeastern India. It is located between 24°40'N and 27°45'N latitude and 89°41'E and 96°20'E longitude. The Indian state of Assam is home to the city of Tezpur. It is located along the northern shores of the mighty Brahmaputra River, which originates in the Himalayas and runs through the region to empty into the delta of Bangladesh. Tezpur lies approximately 175 kilometers northeast of Assam's largest city, Guwahati, and serves as the administrative headquarters of the Sonitpur district. The city is known for its scenic beauty, surrounded by lush greenery, hills, and tea gardens. Tezpur is strategically located at the foothills of the Eastern Himalayas, making it a gateway to the northeastern states and a significant cultural and economic hub in the region. Bioprospecting, hailed by United Nations Development Programme (UNDP) as the 'next-gen green gold', entails exploring natural sources for molecules and genetic information with commercial potential across various industries. The northeastern region of India, often referred to as the "Paradise Unexplored," is renowned for its rich floral diversity, with a plethora of plant species found across its varied landscapes. Northeast India is a treasure trove of medicinal plants, many of which have been traditionally used by indigenous communities for centuries to treat various ailments but it is now that some scientists have started acknowledging its benefits and has re-purposed those diversities into functional materials (Table 2.1). Bioprospecting efforts focus on identifying novel bioactive compounds from these plants for pharmaceutical and nutraceutical applications (Fig. 2.1). Plants such as *Rauvolfia serpentina*, *Acorus calamus*, and *Picrorhiza kurroa* are among the many species studied for their medicinal properties^[1]. The region is also known for its aromatic and essential oil-bearing plants, which possess significant commercial value. Species like *Cymbopogon flexuosus* (Lemongrass), *Curcuma angustifolia* (Wild Turmeric), and *Mentha arvensis* (Wild Mint) are extensively studied for their essential oil content, which finds applications in perfumery, cosmetics, and aromatherapy^[2]. Bioprospecting efforts aim to



identify bioactive compounds with potential pharmaceutical, agricultural, or industrial applications^[3,4]. Northeast India's diverse flora offers a vast repository of such compounds, including alkaloids, flavonoids, terpenoids, and phenolics^[5]. These compounds exhibit various biological activities such as antioxidant, antimicrobial, anti-inflammatory, and anticancer properties, making them valuable targets for drug discovery and development ^[6]. Collaborative initiatives involving local communities, researchers, and policymakers are essential for promoting sustainable bioprospecting practices and equitable benefit-sharing^[8]. Numerous plant species, including plants for medicinal purposes, crops for agriculture, and herbal extracts, have been studied for their use in the engineering of Nanoparticles (NPs). The properties of the synthesized Nanoparticles (Nps) can be considerably influenced by the plant species and extraction procedures used; therefore, it is critical to select acceptable plant materials and protocols. The tiny particles known as nanoparticles, which are usually between one and one hundred nanometres in size, have special qualities because of their small size and large surface area. A larger group of materials known as nanomaterials include bulk materials, nanoparticles, and nanostructures that have been manufactured at the nanoscale to display unique features.



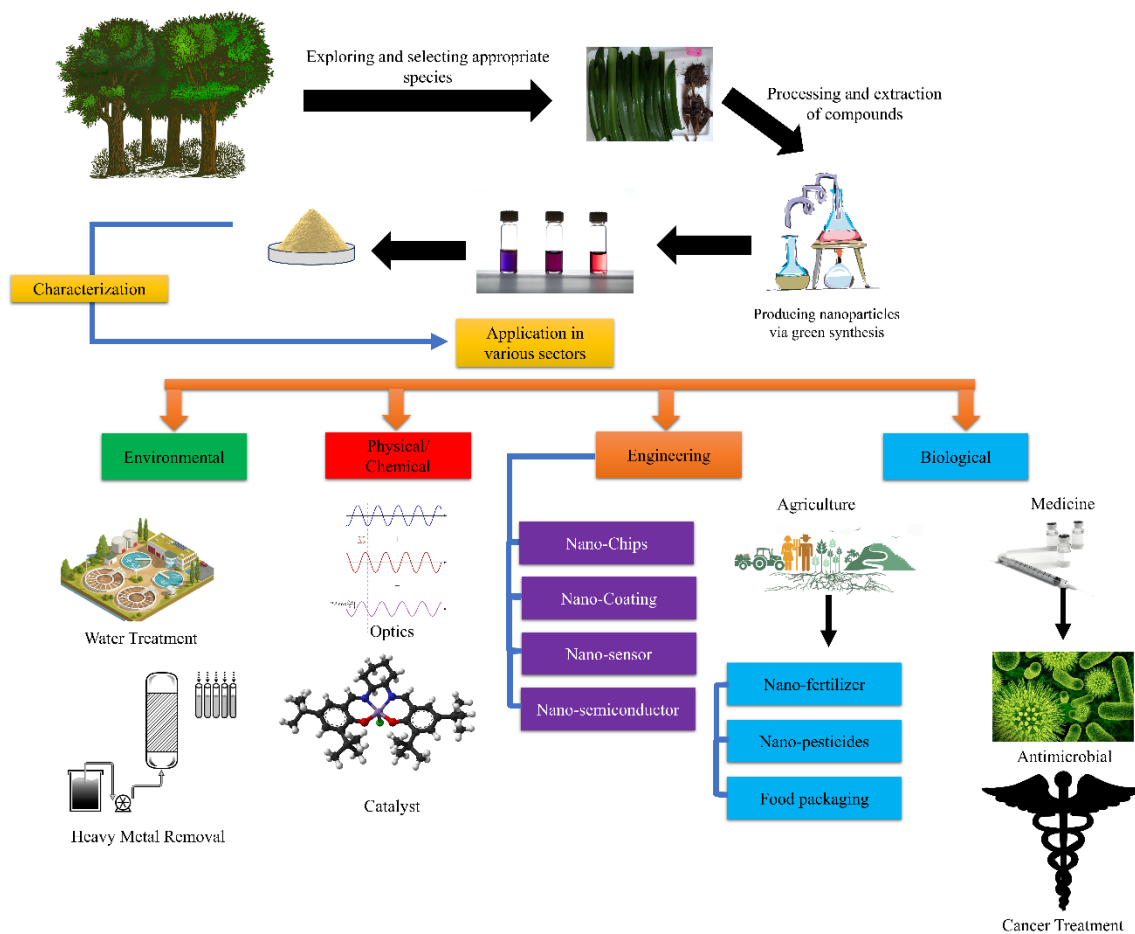


Fig. 2.1. Bioprospecting of Plant parts for the stable synthesis of nanomaterials for its application in various domains

As such, Nanomaterials (NMs) can be of various conformity based on the precursor raw materials used and synthesis parameters. Broadly, based on structure, size, and complexity of the precursor raw materials, Nanomaterials are further classified into:

- Liposomes:** Liposomes are spherical vesicles made of lipid bilayers, like cell membranes. They can encapsulate hydrophilic or hydrophobic compounds within their aqueous cores or lipid bilayers, making them useful carriers for medication delivery and cosmetics^[9,10].
- Dendrimers:** Dendrimers are heavily branching macromolecules having a tree-like shape. They are made up of a central core, many branching units, and functional end groups. Dendrimers are employed in medication delivery, imaging, and nanotechnology because of their variable size, shape, and surface functioning^[11].
- Micelles:** Micelles are self-assembled colloidal structures composed of amphiphilic molecules in a solvent. They have a hydrophobic core and a hydrophilic shell, which allows



them to dissolve hydrophobic medicines or compounds in aqueous solutions. Micelles are widely employed as medication carriers and surfactants in pharmaceuticals and cosmetics [12].

d) **Heterostructures:** Heterostructure nanoparticles are made up of two or more different materials organized in distinct areas or layers. They have distinct optical, electrical, and catalytic capabilities that result from the interfaces between the various materials. Heterostructure nanoparticles have applications in catalysis, sensing, and energy conversion devices [13].

e) **Nanowires:** Nanowires are one-dimensional nanostructures that have large aspect ratios and consistent diameters. These structures may be made of metals, semiconductors, or insulating materials. Nanowires have various applications, including nanoelectronics, photonics, and sensors [14,15].

f). **Nanotubes:** Nanotubes are hollow, cylindrical objects having nanoscale diameters. They can be made of carbon (nanotubes), metals, or metal oxides. Nanotubes have unique mechanical, electrical, and thermal properties and are employed in a variety of applications including composites, energy storage, and nanoelectronics [16].

g) **Core-shell Nanoparticles:** Core-shell nanoparticles consist of a core material encased in a shell composed of a different material. These nanoparticles have potential applications in drug delivery, catalytic processes, and imaging because they combine the strengths of the fundamental and shell materials [17,18].

h). **Janus Nanoparticles:** Janus nanoparticles are asymmetric nanoparticles with two different surfaces or areas. These nanoparticles, which have unique features such as directional self-assembly and controlled release, have uses in medication delivery, catalysis, and optics [19].

i) **Nanocomposites:** Nanoparticles, which usually possess at least a single dimension in the vicinity of the nanometre, are reinforced inside a polymer matrix to create materials known as nanocomposites. Nanoparticles add unique mechanical, thermal, electrical, and barrier properties to the composite material. To create nanocomposites with specific qualities, a variety of synthesis processes are used, including solution mixing, melt mixing, and in-situ polymerization [20]. Nanopolymers are polymer materials having nano-sized dimensions or nanostructured architectures, which provide greater mechanical strength, flexibility, and usefulness than traditional polymers. They are produced utilizing a variety of processes, including controlled radical polymerization, self-assembly, and template-directed synthesis.



Because of their special properties at the nanoscale, nanopolymers are helpful in many fields, such as electronics, coatings, drug administration, and tissue engineering [21]. Fig.2.2. depicts the different possible conformation of NMs based on synthesis parameters and raw materials used as pre-cursors.

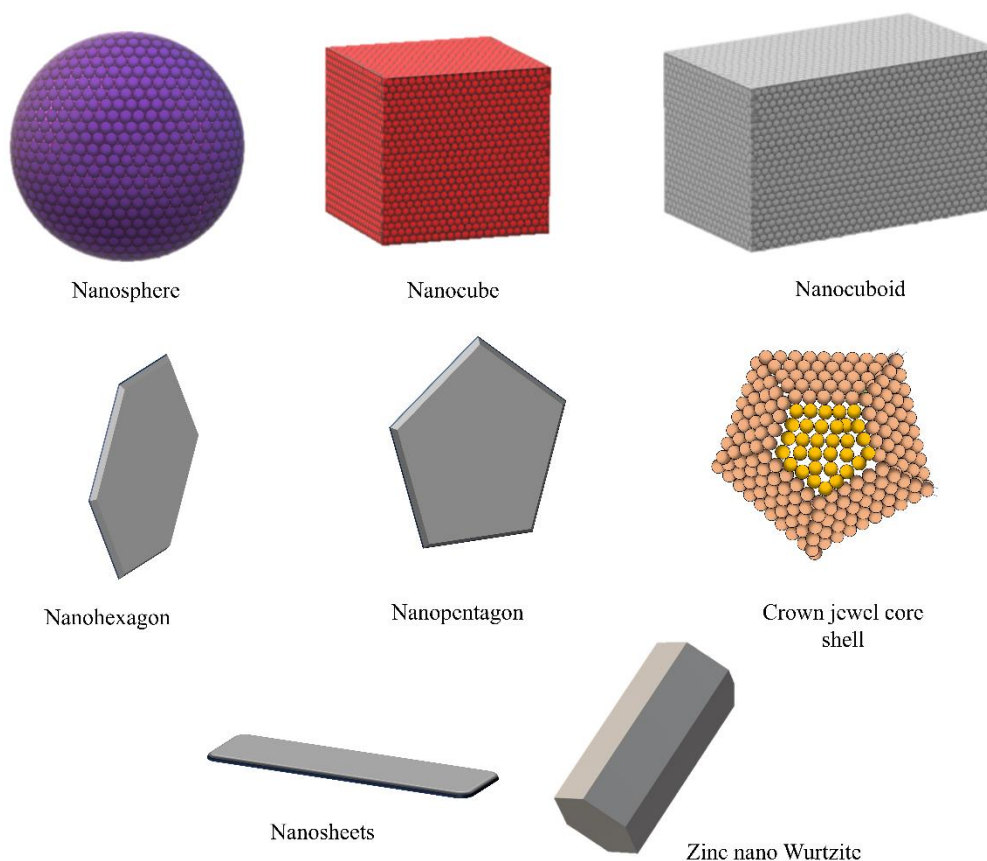


Fig. 2.2. Different structural conformity of engineered nanomaterials influenced by the dynamics of synthesis parameters

2.1. Biological Route for the synthesis of eco-friendly nanoparticles

A viable substitute for conventional nanoparticle synthesis techniques is biological nanoparticle manufacturing or biosynthesis. Biosynthesis is an environmentally friendly process based on green chemistry. Nanoparticle biogenesis is facilitated by bioprocessing, which is allegedly benign, clean, and safe for the environment. These methods enable the production of nanoparticles with the appropriate dimensions, qualities, and use for targets [22,23]. The precise process by which plant extracts function as compounds that reduce



and cap to generate metal nanoparticles, however, is not yet sufficiently supported by data. Photons are transmitted by the photosynthesis Electron Transport System (ETS) in chloroplasts, which affects the creation of metallic nanoparticles. Photons are transmitted by the photosynthetic Electron Transport System (ETS) in chloroplasts, which affects the creation of metallic nanoparticles (Fig. 2.5). Although biological metal nanoparticles are expensive and require harsh chemical reagents for chemical synthesis, their removal efficiency is promising. Consequently, there is a rising need for novel metal nanoparticle combinations and types (such as bimetallic and trimetallic NPs) that can get around these restrictions and yet be useful for environmental cleanup.

2.1.1. Plant-mediated fabrication

Plant extracts (flower, fruit, seed, leaf, stem, latex, resin, and roots) have been successfully employed to produce NPs because they act as stabilizing and/or reducing agents. Plant extracts are prepared using Soxhlet extraction, boiling or dissolving in polar solvents, and filtration. Plant extracts rich in antioxidants are good reducing agents, according to preliminary research, making them a superior option for sustainable synthesis^[26]. Green synthesis includes combining a standardized amount of plant extract (w/v) or metal salts with a predetermined buffering capacity and temperature^[27–29]. The co-reduction method involves simultaneously reducing metal ions from various precursor salts in the presence of a reducing agent. Metal nanoparticles are generated and grow because of reduction processes, which also define their size, content, and form. Reaction kinetics, temperature, pH, concentration, and the reducing agent employed all have a significant impact on the method of synthesis and the characteristics of the final nanoparticles. The colour of the plant extract and metal salt mixture changes to indicate that metal ions have been reduced into nanoparticles^[27]. Particles are then extracted using a step-by-step process of centrifugation and washing, followed by air or oven drying at the proper temperature^[28]. The best reducing and stabilizing agents for green synthesis approaches have been investigated across a range of biological materials^[30–32]. Larger particles are produced when magnetic nanoparticles agglomerate together to form huge groups^[34]. This is caused by a greater surface area compared to volume ratio, strong dipole-dipole interactions, and Van der Waals forces. Nanoparticles can cluster in high-salinity solutions, as those seen in most physiologically relevant media. Agglomeration is influenced by the size and surface of the nanocrystals and can happen quickly or over a few



days. To decrease agglomeration, and increase adsorption capacity, surfactants are used as capping and stabilizing agents throughout the nanoparticle synthesis process. The effects of pH, adsorbent dose, temperature, and phosphate concentration on phosphate adsorption were investigated by Cao et al. [35] utilizing cetyltrimethylammonium bromide (CTAB)-stabilized, inconsistent, sphere FeO nanomaterials that were derived from pine leaf extract. Fig. 2.3. represents the plant extract mediated green synthesis of metal oxide nanoparticles. An endothermic reaction is favoured by the increasing adsorption capacity with heat, which is described by a surge in activation energy [36]. According to research done by Sun et al. [37], encapsulating magnetite nanoparticles with sodium oleate as opposed to polyethylene glycol (PEG 4000) reduces toxicity and increases biocompatibility.

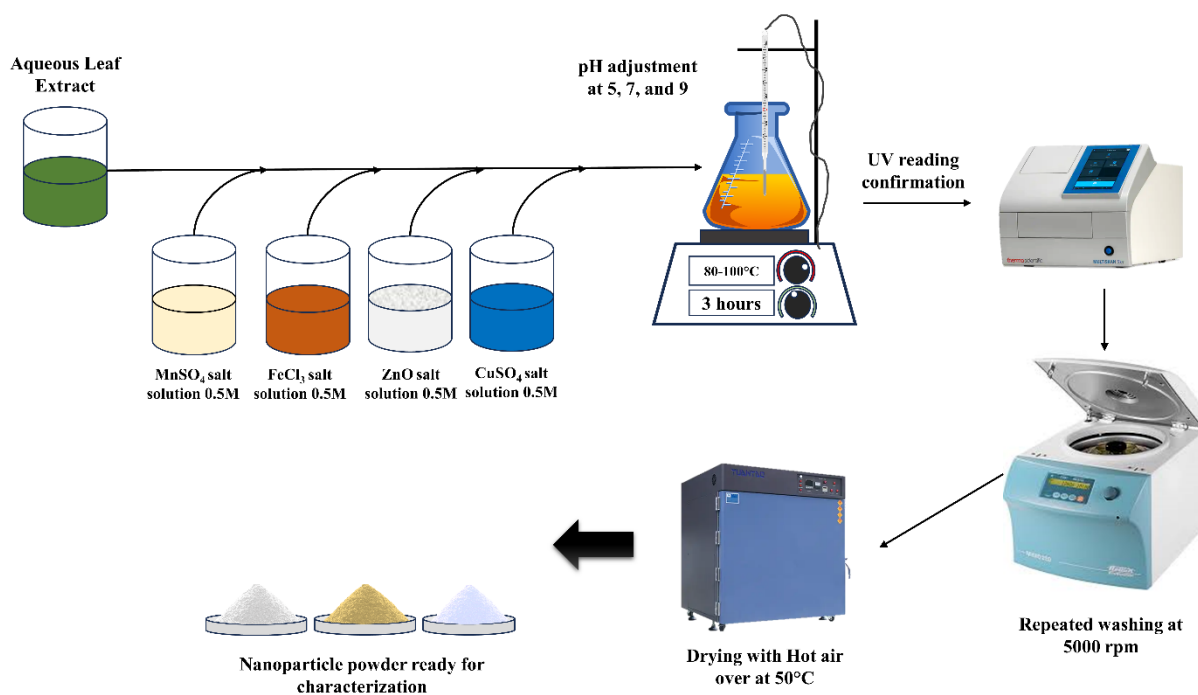


Fig. 2.3. Step-wise process of plant-mediated Green synthesis of metal oxide nanoparticles



Table 2.1. Bioprospecting of Flora of North-East India for Synthesis of Bimetallic Nanoparticles.

Sl.no	Species	Species location	Types of nanomaterials	Application	References
1.	<i>Piper pedicellatum</i> C. DC	Arunachal Pradesh	Ag–Au bimetallic nanoparticles	N/A	Tamuly et al. ^[38]
2.	<i>Mentha piperita</i>	Guwahati Assam	Cu–Ni bimetallic nanoparticles	Antimicrobial efficacy and solar-driven photocatalytic activity	Kalita et al. ^[39]
3.	<i>Ramaria botrytis</i> mushroom	West Bengal India	Ag@Au	4-nitrophenol reduction catalyzed by antioxidant and antibacterial properties	Bhanja et al. ^[40]
4.	<i>P. pedicellatum</i> C.DC	Assam	Ag–Au	Reduction of 4-Nitrophenol by Catalysis	Tamuly et al. ^[41]
5.	<i>Ocimum sanctum</i>	Dibrugarh, Assam	Graphene oxide (GO)-anchored Pd/Cu	Heterogeneous catalyst	Sultana et al. ^[42]
6.	<i>Antidesma acidum</i>	Kokrajhar, Assam	Silver nanoparticles.	Textile organic dye degradation	Basumatary et al. ^[43]
7.	<i>Diplazium esculentum</i>	Silchar, Assam	Silver and anisotropic gold nano-structured	Abatement of perilous organic compounds from wastewater	Sinha et al. ^[44]
8.	<i>Lantana camara</i>	Arunachal Pradesh	Au–Pd alloy nanoparticles	Catalytic activities	Chowdhury et al. ^[45]
10.	<i>Parkia roxburghii</i>	Silchar, Assam	Gold and silver nanoparticles	Photocatalytic and antibacterial activities	Paul et al. ^[46]
11.	<i>Lobaria retigera</i>	Silchar, Assam	Ag–Au nanoparticles	Biocompatible Ag, Au, and Ag–Au conjugated carbohydrates nanoparticles	Borah et al. ^[47]
12.	<i>Ocimum tenuiflorum</i>	Dibrugarh, Assam	Bimetallic Ag–Pd/TiO ₂	Catalyst in Presence of Visible Light Irradiation	Gogoi et al. ^[48]
13.	Pomegranate peels	Tezpur, Assam	Pd–Ag nanoclusters	Catalytic Suzuki–Miyaura coupling reaction.	Bhattacharjee et al. ^[49]



Table 2.2. Common synthesis parameters which influence the structure of Monometallic and Multimetallic Nanoparticles

Sl no.	Type of nanomaterial	Synthesis parameters	Structure	Application	References
1.	Heterobimetallic Au@AgCl and Ag@AgCl@Au	<i>Muntingia calabura</i> aqueous flower extract with microwave oven at 800 W, pH 7, 80 °C, 6 h	Cubical nanoparticles 30 ± 5.0 nm and 50 ± 5.0 nm	Antimicrobial, antitumor, and angiogenesis-promoting properties	Patra et al. ^[50]
2.	Ag/Au bimetallic nanoparticles	Fruit juice of <i>Punica granatum</i> pomegranate, pH7, room temperature, 25°C, 24 h	Alloy and core-shell nanostructures with diameters of 20 and 50 nm	Catalytic breakdown of methyl orange and the 2-, 3-, and 4-nitrophenols	Kumari et al. ^[51]
3.	Ag/Cu bimetallic nanoparticles	Biosynthesis with <i>Leucas aspera</i> aqueous leaf extract, pH5	Alloy nanoparticles 20 nm	<i>In vitro</i> antioxidant potential, Anti-cancer activity against alveolar cancer	Yang et al. ^[52]
4.	Au/Pt bimetallic nanoparticles	<i>Syzygium aromaticum</i> bud-extract	Core shell nanoparticles 13 nm	Catalytic, antibacterial, and antioxidant activities	Sharma et al. ^[22]
5.	Au/Pd bimetallic nanoparticles	<i>Lantana camara</i> flower extract, molar Au/Pd ratio of 4:1.	Spherical alloy nanoparticles of various sizes 5-10 nm, 10-15 nm, 8-22 nm, 14-35 nm, 11-30 nm	Catalytic degradation of dyes	Chowdhury et al. ^[45]
6.	Ag/Fe bimetallic nanoparticles	<i>Salvia officinalis</i> aqueous extract, room temperature,	Core-shell nanoparticles of size 30 nm on an average	Catalytic capability for 4-nitrophenol reduction	Malik et al. ^[53]
7.	Cu/Fe bimetallic nanoparticles	Pomegranate rind	Core-shell spherical nanoparticles of size 60 nm on average	As a nanofertilizer in rice seedlings; hydroponics	Dey et al. ^[54]
8.	Cu/Zn bimetallic nanoparticles	<i>Hibiscus rosa sinensis</i> extract with thermal treatment	50-80 nm	Development of nanocomposites hybrid films with antimicrobial activity.	Singh et al. ^[55]
9.	Au/CuS bimetallic nanoparticles	Solvent-induced self-assembly technique, modified the nanoparticle surfaces with folic acid and doxorubicin encapsulation	6 nm nanoplatform	Multifunctional bionanoplatforms for breast cancer imaging and treatment	Yang et al. ^[56]
10.	Ag-Fe ₂ O ₃ bimetallic nanoparticles	Cabbage peel extract	Core shell nanostructures of size 22.3 nm	Dye degradation and antioxidant properties	Idris et al. ^[57]



11.	Cu/Ni bimetallic nanoparticles	Sugarcane pulp, bagasse, and biochar composite having a hierarchical structure that has been filled with Cu/Ni Nps	Fish net-like structured biochar and well-dispersed 40 nm CuNi nanoparticles provided metal active sites	Catalytic dye removal	Tang et al. ^[58]
12.	Cobalt ferrite bimetallic nanoparticles	<i>Tamarindus indica</i> fruit extract, pH10, 80°C/8 h	13 and 5 nm	Investigation of Magnetic property	Gingasou et al., 2021
13.	Au–Ag bimetallic nanoparticles	different parts of <i>A. leptopus</i> , pH (4-10 ± 0.3) 29 ± 3°C to 70 °C Co-reduction method, simultaneous reduction,	Spherical, triangular, and irregular shapes (8–176) nm	N/A	Ganaie et al. ^[59]
14.	Au@PdAuCu trimetallic core-shell mesoporous nanospheres	Diocetadecyldimethylammonium chloride (DODAC), commercially palladium black (PdB) nanoparticles that copper nitrate (Cu (NO ₃) ₂), palladium chloride (PdCl ₂), and chloroauric acid (HAuCl ₄).	Shell thickness 25 nm, core thickness 40-45 nm	Electrocatalytic application in ethanol oxidation	Lv et al. ^[60]
15.	Fe-Mn bimetallic nanoparticles	Bacterial Auxin complex, pH4.8, 45°C, 5 hrs	Alloy Spherical 26.65-50 nm	Plant biofertilizer	de França Bettencourt et al. ^[61]
16.	ZnO–CuO bimetallic nanoparticles	<i>Sambucus nigra</i> L. extract, pH8, 70 °C for 3 h.	Polygonal shapes with diameters 20 to 130 nm	Cytotoxicity in lung cancer cells	Cao et al. ^[62]
17.	Au–Ag–Pd Trimetallic Nps	Irradiation of combinations of Au, Ag, and Pd colloidal material by laser	Alloy nanoparticles with a diameter 4.4 ± 1.5 nm	Catalyst	Tsai et al. ^[63]
18.	Pt–Ru–Co Trimetallic Nps	Microemulsions procession	Homogenous alloy structure with 2.7 ± 0.6 nm	Electrocatalytic properties	Zhang et al. ^[64]
19.	Sulphur-doped mono-, bi-, and trimetallic nanoparticles trapped in mesoporous carbon	Utilizing thiol-assisted pyrolysis and hydrothermal systems, sulfur-doped mono-, bi-, and trimetallic nanoparticles trapped in mesoporous carbon can be produced.	Heterogenous particle 20-30nm	Enhanced catalytic activity	Tian et al. ^[65]
20.	Pt-Pb-Ru Trimetallic Nps	Metal interfacial diffusion driven effect during high-temperature	15-23 nm	Electrocatalytic oxidation performance of methanol	Liao et al. ^[66]
21.	Palladium/Gold/Silver Trimetallic Nps	<i>Bos taurus indicus</i> /BTI urine	Cubic heterogenous with size 197 nm	Antioxidant and antimicrobial activity, degradation of nitroarenes and azo dyes catalytically.	Sarvalkar et al. ^[67]



22.	Au/Pt/Ag Trimetallic Nps	Reduction of the relevant ions following a quick NaBH ₄ introduction	Spherical 1.5 nm	High rate of reactivity for the aerobic oxidation of glucose	Zhang et al. ^[68]
23.	Trimetallic nanoparticles Pd-Ag-Fe, Fe-Pd-Ag, and Fe-Ag-Pd	Fe ³⁺ , Ag ⁺ , and Pd ²⁺ chemical reduction utilizing hydrazine in an environment of cetyltrimethylammonium bromide	Spherical 15-20 nm	The catalyst that causes formic acid to produce hydrogen.	Khan et al. ^[69]
24.	CNTs-PdAu/Pt Trimetallic Nps	Physical approach, Room-temperature ionic liquids (RTILS)-assisted sputtering approach and then self-decorated on Carbon-Nanotubes (CNTs) in RTILs	~3-3.95 nm	High Electrocatalytic Activity and Stability	Cai et al. ^[70]
25.	NiPdPt Trimetallic Nps	Synthetic chemical route supported on Vulcan carbon, oleylamine, and oleic acid	30-52 nm	Electrocatalysts towards the oxygen reduction reaction	Cruz-Martínez et al. ^[71]
26.	Au/Ag/Pd Trimetallic nanoparticles	An aqueous solution of Gold (III) chloride trihydrate and silver nitrate was refluxed in the presence of cetyltrimethylammonium bromide (CTAB) to create the colloidal dispersions of gold silver bimetallic nanoparticles protected by CTAB.	Core-shell structure with	Sonogashira Pairing Chemistry Facilitators	Venkatesan et al. ^[72]
27.	Shell of Platinum a single layer with palladium and gold (Pt~Pd _{1-x} Aux)	Chemical synthesis with sodium borohydride, Palladium-gold extremely thin nanowires	Alloy Core-shell 2- 50 nm	Electrocatalyst	Koenigsmann et al. ^[73]
28.	Sn-Mn-Fe Trimetallic nanomaterials	The synthetic Chemical route, electronic waste, and waste-printed circuit boards leachate was treated with Disodium Ethylenediaminetetraacetic acid (C ₁₀ H ₁₆ N ₂ Na ₂ O ₈), sodium hydroxide (NaOH), and methyl alcohol	~50 nm, uniform spherical nanoparticles	Improve the yield and grade of cow dung through anaerobic digestion (AD) using it as a biological substrate.	Akar et al. ^[74]
29.	Ca ²⁺ , Fe ²⁺ , and Zn ²⁺	Fabricated on the Maillard reaction products (MRPs), Ca compound (MRPs-Ca), lysine (7.3 g, 50 mmol) in 150 ml of distilled water was heated to 50°C.	<30 nm	Food performance, which enhances the apple's nutritional value (<i>Malus domestica</i> Borkh.)	Yang et al. ^[52]



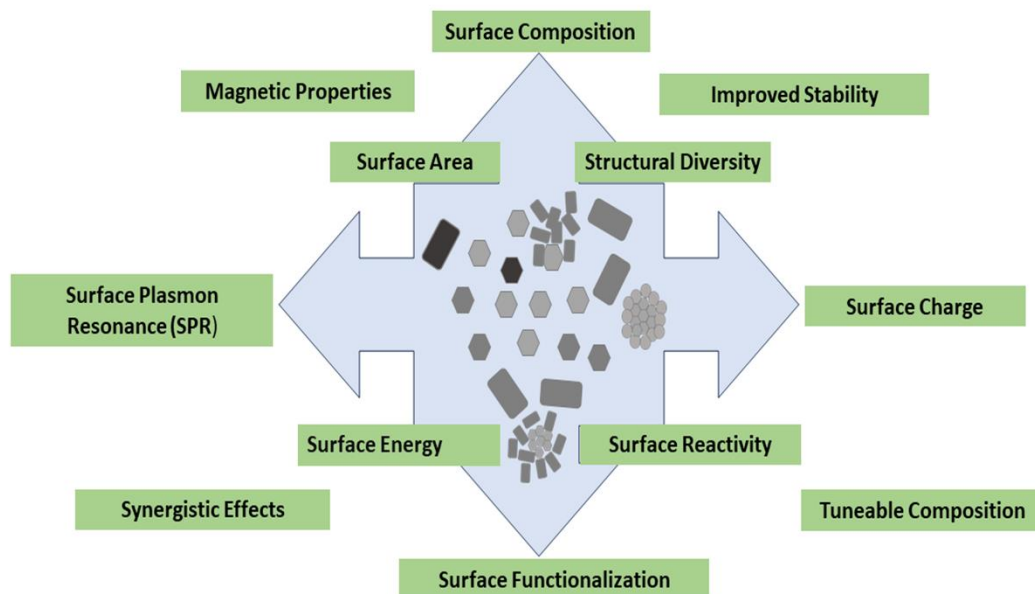


Fig. 2.4. Multi-dimensional properties of Engineered nanomaterials

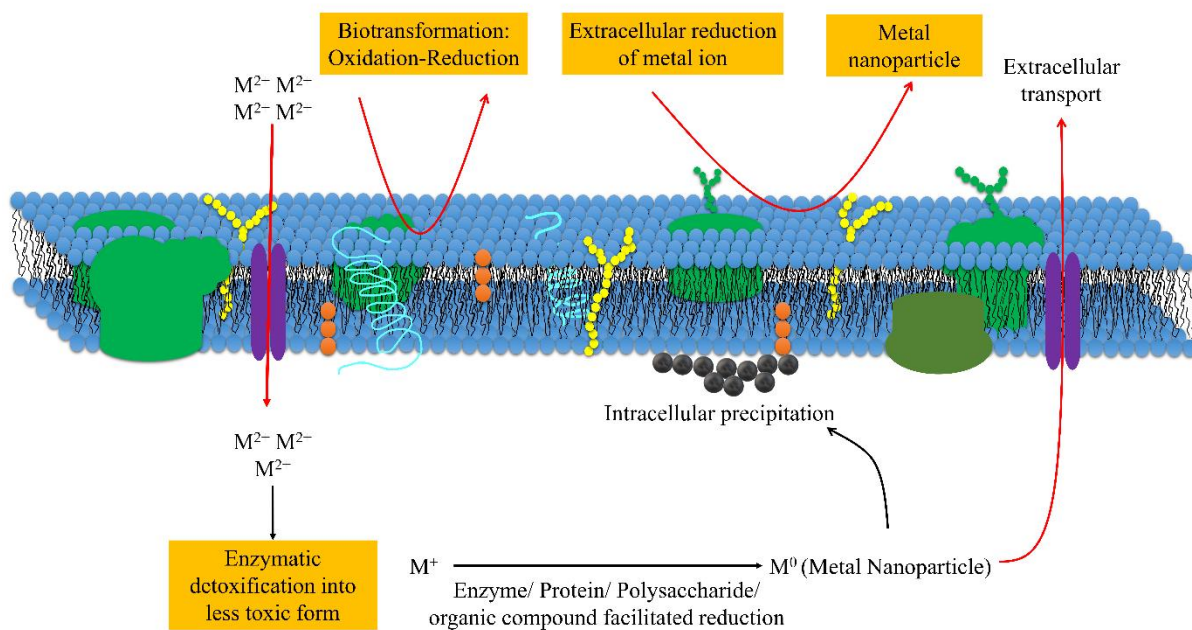


Fig. 2.5. Mechanism of metal ions biotransformation in the extracellular and intracellular membrane



2.2. Factors affecting structural variations

The factors that affect most of the structural variations are the antioxidant potential of plant extracts, Stabilizers, pH, temperature, reaction duration, precursor materials, and RPM all have a significant impact on particle structure.

2.2.1. pH

The production of nanoparticles depends critically on the pH of the process. Like how temperature affects nucleation center formation, pH also has an impact. The amount of nucleation sites increases with pH, leading to a rise in the production of metallic NPs. It has been established that pH influences the shape and size of NPs. The generation of nanoparticles of Au from *A. sativa* at different pH levels was studied by Armendariz et al. [96]. They discovered that at a lower pH level (pH 2), fewer NPs were generated, but that their size was substantially bigger (25-85 nm). They suggested that because Au nanoparticles do not form as many nucleation centers at lower pH levels, they combine to form larger NPs [96]. Conversely, tiny NPs were generated at a bit greater pH range (about pH 3-4). Conversely, tiny NPs were produced at a slightly higher pH (3-4). Studies show that changing the reaction fluid's pH results in a variety of shapes and sizes for the nanoparticles. At lower acidic pH values than at higher levels of pH, larger particles form more readily [97,98].

2.2.2. Reaction Time

Reaction time has been identified as one of the key factors affecting NP shape, along with pH and ambient temperature. Ahmad et al. [99] found that *Ananas comosus* extract reaction time plays a significant role in the production of sphere-shaped Ag nanoparticles. In this instance, it resulted in a quick hue change that took less than two minutes [99]. The aqueous Ag (NO)₃ in the resulting medium drastically decreased in about two minutes, and nanoparticles started to form. For an additional five minutes, the reaction persisted with minimal colour change, yielding round nanoparticles with a median size of 12 nm. Furthermore, Prathna et al. [100] discovered that longer reaction times produced larger particles when *Azadirachta indica* extract of leaves and Ag (NO)₃ were combined.

2.2.3. Temperature

Researchers have found that, although reaction temperature is important in all synthesizes, it also affects the size, shape, and yield of nanoparticles derived from plant extracts [101]. The shape, size, and synthesis rate of nanoparticles—such as triangular, octahedral platelets,



spherical, and rod-like—are all significantly influenced by temperature. At 20°C, triangular nanoparticles were made, and between 30 and 40°C, octahedral nanoparticles with diameters ranging from 5 to 500 nm were created. Furthermore, the sizes of the nanoparticles were noticeably homogeneous and spherical at greater temperatures (about 50–60 °C). A study on the biological synthesis of metallic nanoparticles from *P. eldarica* extracts from bark at varying temperatures was conducted by Iravani and Zolfaghari^[102]. The following temperatures were used for the synthesis: 25, 50, 100, and 150°C. The researchers found that when the temperature climbed, the dimension of the nanoparticle shrank but their production did not. Scanning Electron Micrographs (SEM) of nanomaterials provided evidence for this assertion. Using the biodegradable polymer polyethylene glycol, Fleitas-Salazar et al.^[103] examined the impact of temperature and oxidation on the formation of Ag NPs. They claim that at 100°C, PEG's capacity to decrease silver salt was demonstrated to be enhanced. They found that at 100°C, the functional groups that are part of PEG react violently with silver molecules, forming solid clumps. Ag nanoparticles with a standard particle size of 35 nm were produced utilizing the peel extracts of *Citrus sinensis* at a reaction temperature of 25°C. The average particle size drops to 10 nm when the reaction temperature is raised to 60°C^[104].

2.2.4. Pre-Cursor Materials

The generation of metallic nanoparticles is significantly influenced by the kind and number of biomolecules present in plant extracts. The reduction of metallic ions and the ultimate output of functional nanoparticles are directly influenced by the antioxidant potential of several plant extracts. According to Huang et al.^[105], the amount of sun-dried *Cinnamomum camphora* (camphor) extract from leaves in the response fluid had a major impact on the Au and Ag nanoparticles' generated shapes. By adjusting the amount of Aloe vera leaf extract in the reaction fluid containing chloroaurate ions, Chandran et al.^[106] changed the ratio of gold triangular plates to spherical nanoparticles. The study found that the extract's carbonyl compounds also aided in the formation of particles. The rate at which of nucleation as well as growth of nanoparticles is influenced by the ion concentration of the salt solution^[107,108]. Salts with higher ionic strengths can cause faster nucleation, resulting in smaller nanoparticles with a narrower size distribution. The solubility of the salt precursor in the reaction media impacts its suitability for nanoparticle production. Highly soluble salts can result in more uniform nucleation and smaller nanoparticles, whereas sparingly soluble salts can cause slower nucleation and larger nanoparticles. Table 2.2. summarizes the potential role



of synthesis parameters and pre cursor materials in shaping the multifunctionality of engineered nanomaterials in various fields. The mechanism of nanoparticle generation is influenced by the reduction capacity of metallic ions in salt solution. Greater reduction potentials encourage the decrease of the metal ions through decreased agents, which produces metallic nanoparticles with well-defined sizes and shapes. Certain ligands or coordination molecules present in the reaction media can combine with certain metal ions in salts to create complexes. These compounds can stabilize crystal facets during nanoparticle growth, resulting in the preferential production of specific geometries like nanocubes and nanorods.

2.3. Characterization

Material characterization is part and parcel of particle engineering. To have a clear-cut idea of the characteristic feature of the engineered nanoparticles, UV-visible spectroscopy is needed for metal oxides (e.g., zinc oxide, titanium dioxide), to have unique absorption spectra due to quantum confinement effects and surface interactions. The bandgap energy influences the wavelength of light absorbed by nanoparticles and is important in many applications, such as solar cells, photocatalysis, and sensors. Zhang et al.^[111] studied the bandgap of SnO₂ nanoparticles synthesized using a sol-gel technique. They used UV-Vis's spectroscopy and the Tauc plot method to calculate the bandgap, which was 3.7 eV. Like this, Liu et al.^[112] investigated the bandgap of hydrothermally produced zinc oxide (ZnO) nanoparticles. They discovered the bandgap to be 3.2 eV using UV-Vis spectroscopy and the Tauc plot approach. Li et al.^[113] studied the bandgap engineering of TiO₂ nanoparticles to improve photocatalytic activity, whereas Zhang et al.^[114] researched the bandgap tuning of ZnO nanoparticles to improve sensor performance. Using the Tauc plot approach, you may determine a material's bandgap energy (E_g). The Tauc equation connects the absorption coefficient (α) to photon energy (hv) using the following expression:

$$\alpha \propto (hv - E_g)^n$$

The bandgap energy is represented by E_g in this equation, while the incident light frequency is denoted by ν , Planck's constant is h , and n varies according to the permitted electronic transitions, which are generally 1/2 for direct transitions and 2 for indirect transitions. Similarly, DLS is a technique for measuring particle size distribution in suspension or solution that uses the Brownian motion principle. Brownian motion, or the random motion of particles suspended in a solution, causes the intensity of dispersed light to fluctuate over



time^[115]. This, X-ray photoelectron spectroscopy (XPS) is a method for figuring out a material's chemical state and elemental composition. This information reveals the chemical makeup, chemical bonding, and oxidation states of the elements present in the substance^[116]. High-Resolution Transmission Electron Microscopy (HR-TEM) is a strong method for material characterization that investigates nanomaterials' precise structure and shape. HR-TEM enables researchers to see materials at the atomic level, revealing important details about their crystalline structure, flaws, and surface properties. Moreover, HR-TEM can be combined with methods like energy-dispersive X-ray spectroscopy (EDS) and selected area electron diffraction (SAED) to learn more about the phase, composition, and elemental distribution within nanomaterials. Field Emission Scanning Electron Microscopy (FE-SEM) is an effective technique for characterizing materials at the micro- and nanoscale. It combines high-resolution photography with the capacity to analyze surface shape, composition, and elemental distribution. In addition to imaging, FE-SEM can do elemental analysis using energy-dispersive X-ray spectroscopy (EDS) or X-ray microanalysis. This technique identifies the characteristic X-rays generated by the sample when blasted with electrons, which provide information about the material's elemental makeup and distribution. EDS can detect and map the presence of different elements, allowing researchers to link chemical composition to surface morphology. A common technique for characterizing porous materials is BET (Brunauer-Emmett-Teller) analysis^[117], which identifies the porosity and specific surface area of the material. Brunauer, Emmett, and Teller developed BET analysis in 1938, which is based on the physical adsorption of gas molecules onto the surface of a solid substance. In recent years, NMR spectroscopy has been widely used to characterize nanomaterials, polymers, catalysts, and biomaterials. Powder X-ray diffraction (XRD) is a strong method used to characterize powdered samples. It describes the crystalline structure, phase composition, and crystallographic properties of materials^[118]. FTIR is used to detect the existence of functional groups (such as C-H, O-H, and C=O) in organic and inorganic substances. Structural analysis reveals molecular structure, conformational changes, and intermolecular interactions in material that can be used to determine the concentration of individual chemicals in mixtures. It is commonly employed in polymer analysis to investigate chain branching, crosslinking, and polymerization processes^[119]. Zeta potential is an important measure for determining the stability of colloidal dispersions. Higher absolute zeta potential levels often indicate higher particle repulsion, resulting in increased dispersion stability. It reveals information on the surface charge of nanoparticles and colloidal particles,



which determines their interactions with other particles and surfaces. Zeta potential measurements are important in the formulation of colloidal systems such as emulsions, suspensions, and nanoparticles because they help optimize formulation parameters to obtain desired attributes and stability^[120]. Thermo-gravimetric analysis (TGA) is used to determine the starting, peak, and end temperatures of thermal breakdown processes in materials. It aids in determining the thermal stability of polymers, composites, catalysts, and other materials under varying conditions. TGA can measure the volatile content, moisture, and other volatile components found in materials. TGA data can be used to study the kinetics of degradation reactions and understand their mechanisms. TGA is used in the pharmaceutical, polymer, and ceramic industries to regulate quality and optimize formulations^[121]. pH ZPC is critical for developing surface modification procedures, such as functionalization or coating, that modify the surface charge and characteristics of materials, and the colloidal stability of suspensions and nanoparticles by regulating the electrostatic interactions between particles and the dispersion medium. pH ZPC influences the adsorption behaviour of ions, molecules, and biomolecules on material surfaces, impacting processes such as kinetics and selectivity, an impact on the environmental fate and transit of materials, and influencing interactions with soil, sediments, and aquatic systems^[120].

2.4. Multimetallic Nanoparticles (MMNPs)

The first report on using plant-based systems for mixed metal NP biosynthesis was published in 2007 by Haverkamp et al^[23]. The researchers produced Au-Ag-Cu alloy nanoparticles (~5-50 nm) *in vivo* using seeds from *Brassica juncea* plants Using an extract made with water of *Lamii albi flos*, Au/Pt/Ag trimetallic NPs have been produced in an easy and eco-friendly way^[145]. It was reported that *Meliloti officinalis* extract was used in the eco-friendly preparation of Au-ZnO-Ag trimetallic Nanoparticles (~20 nm)^[146]. In a different study, Vaseghi et al.^[147] described a dependable method for the synthesis of Cu/Cr/Ni trimetallic oxide nanotechnology using aqueous leaf extracts from *Froriepia subpinnata* and *Eryngium campestre* at mild temperature conditions. These NPs demonstrated good antibacterial activity against *Staphylococcus aureus* and *E. coli*. The ideal parameters to produce multimetallic nanomaterials using *E. campestre* leaf extract comprised a metal salt-to-leaf extract concentration ratio of 2.38, producing 73%, and a 3-minute reaction duration at 34 °C. A metal salt-to-leaf extract ratio of 1.07 and 3 minutes at 40 °C were equivalent values for *F.*



subpinnata leaf extract. Using modeling software, it was determined that 72% of the salt was converted into trimetallic oxide nanoparticles (NPs) [147]. By altering the phytochemical makeup, extracts from *Aegle marmelos* (leaf extract) and *Syzygium aromaticum* buds were used to create green-fabricated Ag-Au-Pd trimetallic NPs (~8-11 nm) in 10 minutes under ambient conditions [148]. Polymeric nanoparticles have been used to protect functional foods (nutraceuticals) from the gastrointestinal tract, as well as to create nanoemulsions of omega-3 fatty acids and oil-in-water nanoemulsions (e.g., triglycerides with vitamin D, astaxanthin, or β -carotene). These NPs showed effective antibacterial properties against Gram-negative bacteria like *E. coli* in addition to promising catalytic properties for the glucose oxidation process; the high catalytic activity was probably caused by the electronic transfer of charge influence from nearby elements in trimetallic NPs, which served a crucial role [148].

In the food industry, ZnONPs, SiO₂ NPs, and TiO₂ NPs are used to thicken, colour, clarify, and regulate dust fluidity. AgNPs and ZnONPs are utilized to extend the shelf duration of many products due to their bacteriostatic properties, while FeONPs are used for enhancing meals. As the name suggests, monometallic NPs consist of just one element (Au, Pt, or Pd), while bi- and tri-metallic NPs (Au/Ag, Pt/Pd, Fe/Ag/Pt, and Au/Fe/Ag) consist of two or three metals, respectively. When a second and third metal are added to the nanoparticles combination, bi- and tri-metallic nanomaterials have superior and tuneable features that can enhance enzymatic activity as well as selectivity when compared with single metallic NPs [150]. A third metal's (secondary metal's) catalytic activity may be increased by the metallization of NPs. The structure, size, and form of particles in bi- and trimetallic nanoparticles (NPs), including heterodimers of two or more metals, alloys, and core-shells, are influenced by the preparation circumstances [151,152].

Additionally, the individual and combined catalytic effectiveness of mono-, bi-, and trimetallic NPs was investigated. On the other hand, bi- and trimetallic NPs were discovered to have better catalytic properties than monometallic NPs in earlier research [151]. When a single metal alloy is combined with additional metals to create bi- or trimetallic nanoparticles (NPs), the resultant material's catalytic properties are superior to those of pure metals. Bi- and tri-metallic NPs with the desired size, structure, and shape are prepared using a variety of techniques, which also affect the material's properties. These techniques include electrochemical reduction, microwave microemulsion, simultaneous precipitation, pyrolysis, hydrothermal, sol-gel, solvothermal processes, and combustion [156,157]. Metallic nanoparticles'



antimicrobial properties Fig. 2.4. represents the multidimensional properties of metal nanomaterials for its wide applications in catalysis, agriculture, biomedicines etc.

2.5. Applications of Nanomaterials in Environment

2.5.1. Agriculture

In recent years, there has been increasing interest in the application of nanomaterials in various fields, including agriculture ^[158]. Nanotechnology, which involves the manipulation and control of matter on the nanoscale, offers a wide range of possibilities for improving agricultural practices. With the use of bimetallic nanoparticles, the scope of nanotechnology in agriculture is even more promising. Bimetallic nanoparticles refer to nanoparticles that are composed of two different metals. These nanoparticles have unique properties that make them highly suitable for various agricultural applications. Bimetallic nanoparticles' ability to identify diseases quickly is one of their main advantages in agriculture. Plant infection diagnostic probe sensitivity can be significantly increased by using biosensors coated with bimetallic component nanoparticles, such as Au-Ag or Cu-Ti ^[159,160]. Because of this, plant pathologists and farmers may identify illnesses early on and take prompt action to control them. Additionally, plant disease control can directly apply bimetallic nanoparticles as antibacterial agents. Such nanoparticles have been shown to reduce bacteria and fungi that cause plant pathogenicity, offering a more efficient and environmentally responsible method of disease control. Moreover, bimetallic nanoparticles can also be encapsulated with antimicrobial chemicals, offering a controlled release of the chemical and further enhancing its efficacy. In addition to disease detection and management, bimetallic nanoparticles have the potential to improve crop yield and enhance soil fertility. For example, by incorporating bimetallic nanoparticles into fertilizers, nutrient absorption and utilization by plants can be enhanced. This can lead to increased crop productivity and improved soil health. Furthermore, bimetallic nanoparticles can also be used for the remediation of contaminated soils. Their unique catalytic properties can facilitate the degradation and transformation of pollutants, detoxifying the soil and making it suitable for agricultural purposes. Overall, the scope of bimetallic nanoparticles in agriculture is vast and promising. Their ability to enhance disease detection, provide effective disease management, improve crop yield, and remediate contaminated soils makes them valuable tools in sustainable agriculture ^[69]. Additionally, bimetallic nanoparticles can contribute to the preservation of food commodities. By



incorporating bimetallic nanoparticles into packaging materials, the shelf life of agri-foods can be extended. This can help reduce food waste and improve food safety, ensuring that consumers have access to high-quality and safe agricultural products. In conclusion, the scope of bimetallic nanoparticles in agriculture is extensive. Their applications range from disease detection and management to improving crop yield, soil fertility, and food preservation.

The utilization of bimetallic or multimetallic nanoparticles in agriculture holds great potential for revolutionizing the industry. The need for reliable weather forecasts in the quickly evolving world of today cannot be emphasized. The scope of bimetallic nanoparticles in agriculture is vast and promising ^[161–163]. Their potential to enhance disease detection, provide effective disease management, improve crop yield, remediate contaminated soils, and extend the shelf life of agri-foods makes them valuable tools in sustainable agriculture. Lack of essential elements including iron (Fe), zinc (Zn), manganese (Mn), copper (Cu), boron (B), and molybdenum (Mo) in sufficient amounts for plant absorption results in a lack of soil micronutrients. To address soil micronutrient insufficiency, a variety of remediation solutions are used, such as micronutrient fertilizers, soil amendments, and biofortification approaches. Furthermore, the use of micronutrient-efficient crop cultivars and precision agriculture approaches can improve micronutrient utilization while reducing environmental effects ^[165,166]. Fig. 2.6. represents how metal nanomaterials can be re-purposed for the betterment of the environmental issues (SDGs).



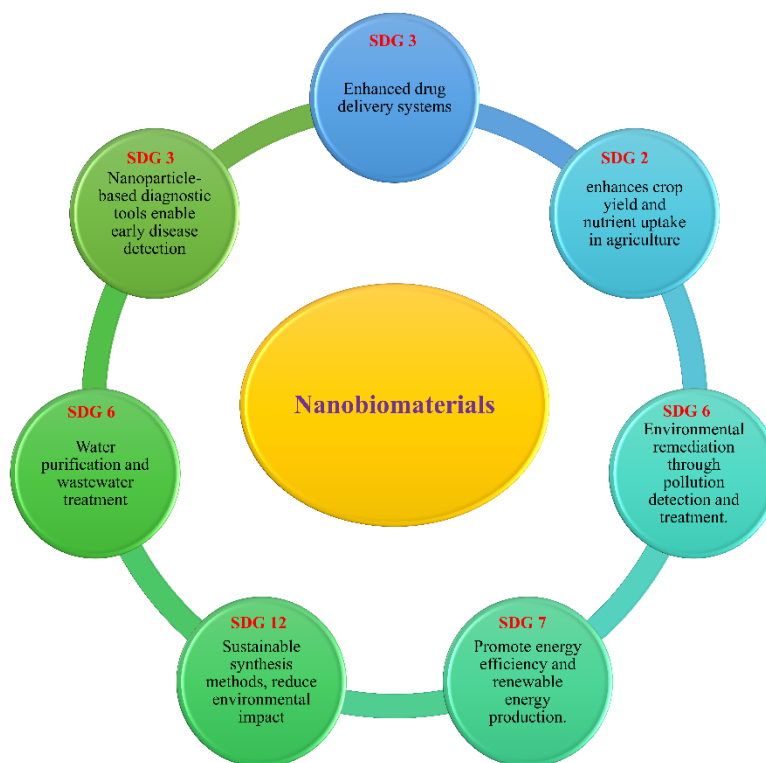


Fig. 2.6. Prospects of Eco-friendly nanobiomaterials in fulfilling Sustainable Development Goals (SDGs)

To reduce nutritional loss, a process known as and pollution of water and air, plant nutrients known as nanofertilizers are composed entirely or primarily of nanostructured formulation(s) [169]. These formulations can accurately and softly release active molecules into the soil. Nanofertilizer (NFs) are an excellent foundation for creating innovative and sustainable nutrition delivery systems due to their enormous surface area concerning volume ratio, which gives them superior efficacy, effectiveness, accessibility, and utilization compared to Chemical Fertilizers (CFs) [170]. According to Baral et al [171], their composition can also facilitate effective crop uptake, the restoration of soil fertility, ultrahigh absorption, enhanced photosynthesis, increased production, decreased soil toxicity, less use frequency, improved plant health, and decreased environmental pollution. Fig. 2.7. represents the sustainable advantages of using plant derived nanofertilizers over chemical fertilizers.



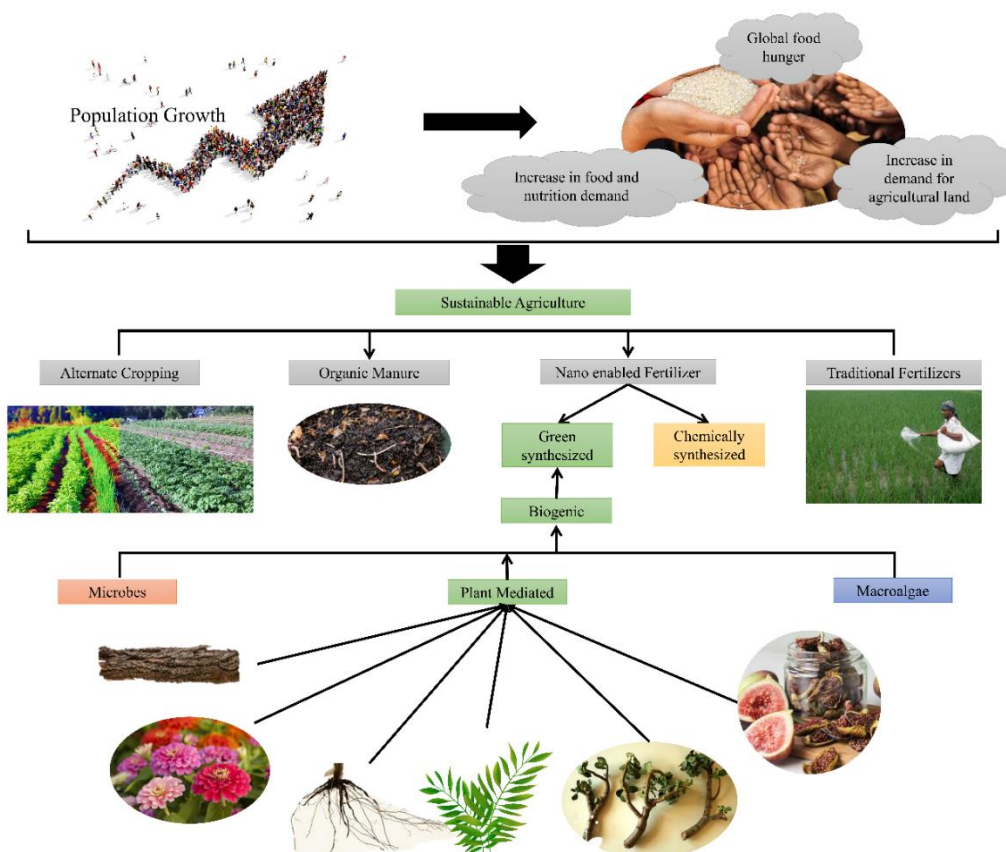


Fig. 2.7. Plant derived nano-enabled benign fertilizers for sustainable agriculture

2.5.2. Biomedical Applications

Without sufficient medical rationale, antibiotics are frequently prescribed to treat infectious disorders, which is contributing to the rising issue of bacterial resistance [175,176]. Because of their resilience to heat, environmental responsibility, and stability in challenging processing environments, alternate antibacterial agents are becoming more and more attractive for the treatment of infectious diseases. Because of their large surface area-to-volume ratio, metallic nanoparticles (NPs) can interact with bacteria and biofilms in a targeted antibacterial manner at low doses. In the last few years, new antimicrobial therapies—such as metallic nanoparticles and macromolecules—have shown to be incredibly successful in combating dangerous microorganisms. Potential antibacterial qualities can be found in metal nanoparticles such as zinc (Zn), iron (Fe), silver (Ag), copper (Cu), gold (Au), gallium (Ga) and palladium (Pd). Aluminium (Al_2O_3), iron (Fe_3O_4), titanium (TiO_2), copper (CuO), zinc (ZnO), and cobalt are examples of metal oxide nanoparticles (NPs). Van der Waals forces,



hydrophobic interactions, and electrostatic attraction are three ways that NPs might breach bacterial cell walls ^[177,178]. Different nanoparticle forms combat germs in different ways. They produce reactive oxygen species, and radicals, deactivate proteins and DNA, generate oxidative stress, and alter gene expression levels by generating pores in the bacterial cell membrane ^[179,180]. To ascertain the safety and effectiveness of nanomaterials employed in biomedical applications, biocompatibility testing is essential.

Nanomaterials interact with many biological components, including blood, cells, and the immune system, necessitating a detailed assessment of their biocompatibility. Hemocompatibility is the compatibility of nanomaterials with blood components, specifically red blood cells (RBCs) and platelets. Nanomaterial-induced haemolysis, platelet aggregation, and coagulation cascade activation are important criteria to consider when ensuring minimal deleterious effects on blood components^[181]. Cytocompatibility testing focuses on the interaction of nanomaterials with cells. Cell viability, proliferation, and morphology are routinely used to test nanomaterial cytotoxicity. To further understand nanomaterial-cell interactions, researchers are also looking into cellular absorption, intracellular localization, and potential genotoxic effects. Immunocompatibility testing evaluates the effect of nanomaterials on the immune system. Nanoparticle-induced immunomodulation, inflammation, and allergic responses are all important factors. Fig. 2.8. represents the possible futuristic biomedical and nutritional applications as formula-based feed for animals and plants.



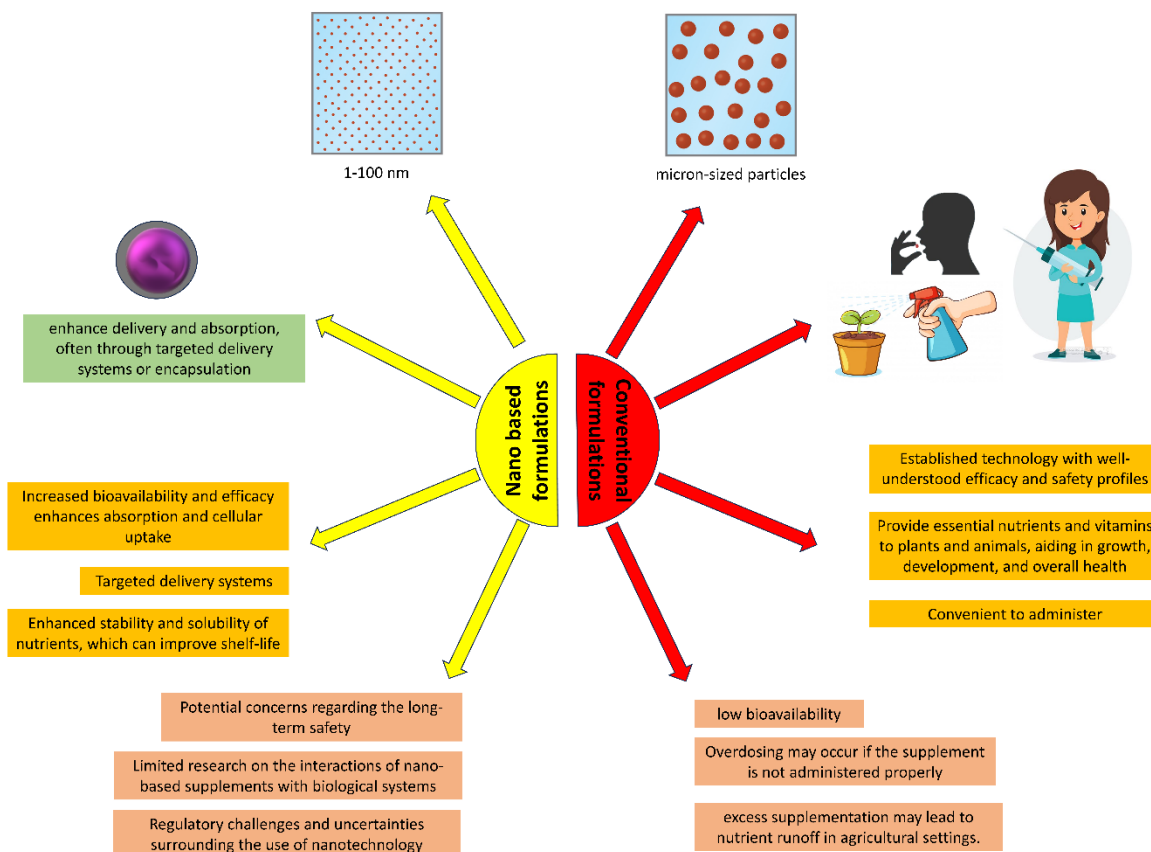


Fig. 2.8. Futuristic applications of nanomaterials as potent formulations for plants and animals

Immunocompatible nanomaterials generate a modest immunological response and interact well with immune cells including macrophages and lymphocytes ^[181]. Several studies have shown that surface chemistry, size, and shape all play important roles in influencing nanomaterial biocompatibility ^[182]. Functionalization techniques, such as covering nanomaterials with biocompatible polymers or changing the surface charge, can improve their biocompatibility ^[183–185]. Because of their distinct physicochemical properties, nanomaterials are useful in many different biomedical applications. It is necessary to comprehend the behaviour of these substances in tissues that are alive, including absorption, distribution, metabolism, elimination (ADME), and toxic effects, to ensure their safe and efficient usage. This is especially important for land disposal. When it comes to risk assessment and regulatory decision-making, Quantitative Structure-Activity Relationship (QSAR) models offer helpful insights into the interaction between nanomaterial properties



and biological repercussions. The quantity, size, charge on the surface, and surface chemistry of nanoparticles influence their incorporation in living tissues, which is primarily responsible for their absorption into the body. Surface changes can increase or decrease absorption, altering tissue biodistribution ^[186-188].

Nanomaterials can spread throughout the body after being absorbed via circulatory or lymphatic channels. Size-dependent distribution to certain organs and tissues has been reported, with smaller nanoparticles having a wider distribution ^[188]. Metabolic activities can change the chemical composition and characteristics of nanomaterials, influencing their biocompatibility and toxicology. Enzymatic degradation, oxidation, or conjugation processes can all occur during nanomaterial metabolism ^[189]. Nanomaterials can be eliminated via renal excretion, biliary excretion, or reticuloendothelial clearance. Size, surface chemistry, and surface change all influence removal kinetics, with smaller nanoparticles clearing faster. Nanomaterial toxicity is multifactorial and is determined by a variety of factors such as size, shape, surface characteristics, and dosage. Quantitative structure-activity relationship (QSAR) models link nanomaterial properties to biological reactions, facilitating toxicity prediction and risk assessment ^[190,191]. Proper land disposal of nanomaterial-containing trash necessitates a thorough risk assessment to mitigate any environmental and human health risks. QSAR-based techniques are excellent tools for forecasting nanomaterial destiny and behaviour in the environment, which can help with regulatory decision-making and risk management ^[192].

2.6. Stability, Risk Assessment and Regulatory Policies

The resilience and activity of nanoparticles of metal in the environment can be impacted by interactions with biological surfaces or microbial communities ^[204]. Metal nanoparticles can become immobile and persist longer in aquatic environments when they are deposited on soil surfaces. The life cycle assessment (LCA) of nano biomaterials gives a complete understanding of their environmental impact over their full life cycle ^[205]. According to International Organization for Standardization (ISO) 14040/44 ^[209], LCA involves four stages: the defining of the goal and magnitude, the Life Cycle Impact Assessment (LCIA), the life cycle inventory analysis, and the interpretation of the findings. The life cycle assessment (LCA) of nanomaterials is critical for quantifying their carbon footprint and comprehending their environmental implications across their whole lifespan ^[210]. Fig. 2.9. depicts the LCA of



engineered nanomaterials for circular economy. Data is collected at each stage of the life cycle, including manufacture, transportation, usage, and disposal. Inventory data is gathered and utilized to analyze the potential environmental implications of nanomaterials. This includes examining variables like greenhouse gas emissions, energy usage, resource depletion, and toxicity. Impact assessment approaches, such as the ReCiPe and USEtox models, are widely employed to measure these effects [211]. The environmental impacts discovered during the impact assessment are normalized and weighted to provide a comprehensive picture of the nanomaterials' overall environmental performance.

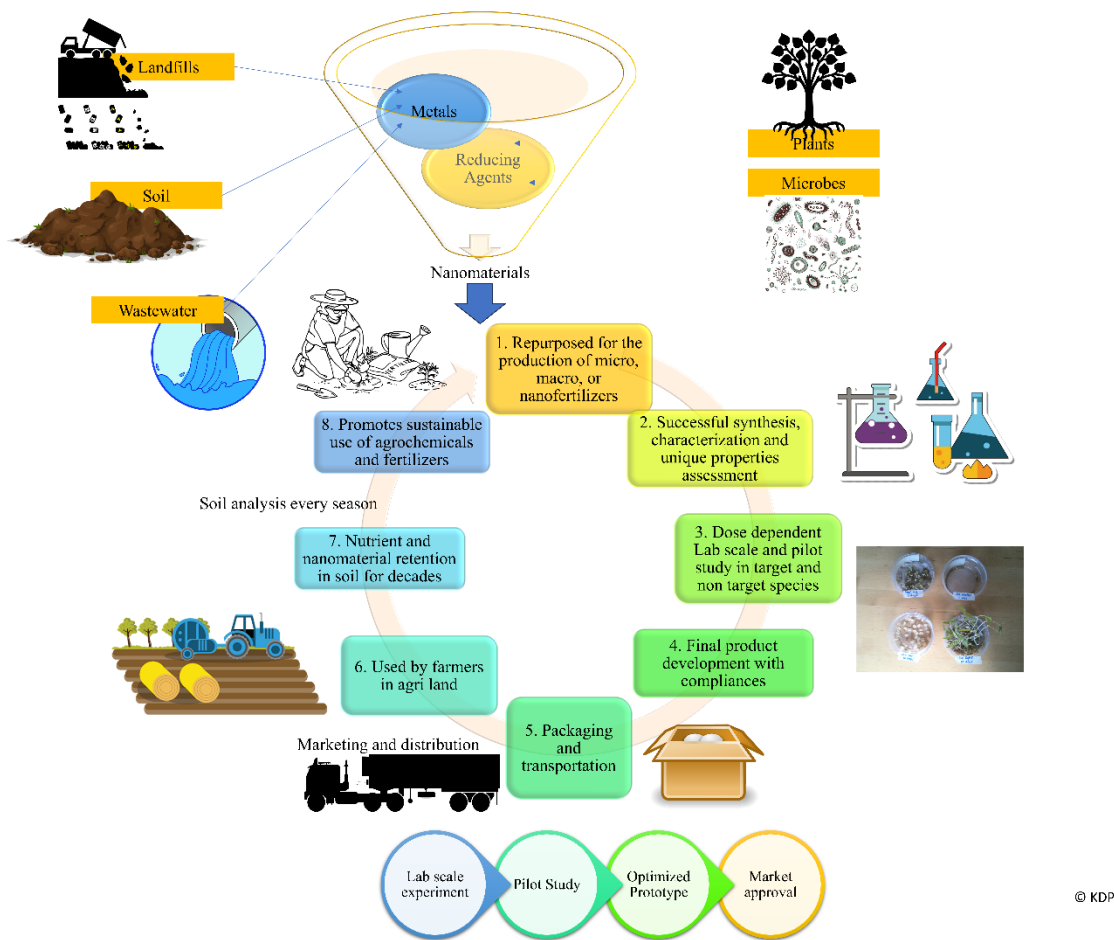


Fig. 2.9. Reusability of metal and electronic wastes for Cradle-to-grave (LCA) impact assessment

In this regard, several regulatory agencies are embracing difficulties in this direction, such as the International Standard Organisation (ISO), the Organisation for Economic Cooperation and Development (OECD), and the US Food and Drug Administration (USFDA). While organizations like the OECD and ISO simply offer recommendations and advice to regulatory



organizations, agencies like the USFDA strictly enforce laws about soil. Different strategies are used by OECD and non-OECD countries to regulate nanotechnology in the feed, food, and agriculture sectors ^[219,220]. REACH (Registration, Evaluation, Authorization, and Restriction of Chemicals) ^[221] is the main EU law that addresses the use of nanomaterials in food additives and supplements, plant protection products, and materials that meet food (European Commission, 2013) ^[222]. While other non-EU countries have non-binding guidelines with non-legal principles, only the EU and Switzerland have effectively implemented globally nano-specific legislative measures, mostly for the food production, agriculture, and feed sectors ^[223]. It is imperative to underscore, meanwhile, that nanoparticle-based treatments for agricultural applications are not proliferating and are facing challenges in reaching the market because of regulatory ambiguities and divergent views globally. The development of regulatory regulations addressing biosafety problems should prioritize risk evaluation and risk management. Moreover, global public discourse on ideas and perspectives would help address successful regulatory initiatives.



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